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Complex formation of Cr^{3+}, Mn^{2} ions using (E)-1-(((3-aminophenyl)imino)methyl)naphthalene-2-ol

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Abstract Metal complexes of Cr(III), Mn(II) of the Schiff base derived from (E)-1-((3-aminophenyl)imino)methyl)naphthalene-2-ol have been prepared and characterized on the basis of physical characteristics, micro-analytical data(CHN), molar conductivity, magnetic moment measurements, Mass spectra, ^{1}HNMR, IR and UV-Vis spectrum data. The elemental analysis data showed the isolated complexes are in 1:1 [M:L] ratio .The obtained molar conductance values revealed the complexes are nonelectrolyte in nature. The results of magnetic moment measurements showed that, the complexes of Cr(III), Mn(II), have unpaired electrons. The infrared spectral data displayed the main coordination sites of (*E*)-1-((3-aminophenyl)imino) methyl)naphthalene-2-ol towards Cr(III), Mn(II) ions. The electronic spectral results of the Schiff base ligand and its complexes suggest that, the Cr(III), Mn(II) complexes have octahedral and tetrahedral structure.

Keywords: Schiff base, Complexes, (E)-1-(((3-aminophenyl)imino)methyl)naphthalene-2-ol , 2-hydroxy-1-napthylaldehde ,m-phenylenediamine.

تحضير معقدات Cr(III), Mn(II). Ni(II), Cu(II) مع مرتبط (E)-1-(((3-أمينو فينايل)) أمينوميثايل نفثالين -2-أول

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الملخص تم تحضير مرتبط قاعدة شيف من 2-هيدروكسي -1- نفثالدهايد مع ميتا- فينيايلين داي أمين وتمت دراسته بواسطة التقنيات مثل التحليل العنصري والأشعة فوق بنفسجية والأشعة تحت الحمراء والرنين النووي المغناطيسي ومطياف الكتلة، وحضر منها متراكبات لقواعد شيف بتكثيفها مع أيونات Mn(II) ،Cr(III). وتم تحديد الاشكال الفراغية للمتراكبات بواسطة الطرق الطيفية والمغناطيسية، وإقترحت جميع المتراكبات ثماني السطوح و رباعي السطوح.

الكلمات المفتاحية: قاعدة شيف، معقدات،(E)-1-(((3- أمينو فينايل)) أمينوميثايل نفثالين -2-أول ، 2-هيدروكسي -1-نفثالدهايد، ميتا-فينيايلين داي أمين .

Introduction

Schiff bases are group of compounds named after Hugo Schiff, who described the Schiff bases as the products of the reaction between aldehydes and amines in 1864[1,2]. Schiff bases also are called azomethines or imines. Schiff bases are characterized by containing the -N=CH- (imine) group. The general formula for these compounds is $R_1HC=N-R_2$, (where R_2 is an aryl or alkyl group and R1 is an aryl group[3].

Schiff bases prepared by an acid catalysed condensation reaction between a carbonyl compound (aldehyde or ketone) with a primary amine in refluxing alcohol through a nucleophilic addition, which leads to the formation of a hemi-aminal, and followed by dehydration to generate an imine[3,4].

Schiff bases are generally monodentate, bidentate, tridentate, tetradentat or polydentate ligands capable of forming very stable complexes with transition metals. They can only act as coordinating ligands if they bear a functional group ,usually the hydroxyl, sufficiently near the site of condensation in such a way that a five or six membered ring can be formed when reactin with a metal ion[5][6].

The importance of Schiff base complexes for bioinorganic chemistry, biomedical applications, supra molecular chemistry, catalysis and material science, separation and encapsulation processes[7,8] , Metal complexes of Schiff-base have played a central role in the development of coordination chemistry[9] , Their metal complexes have been widely studied because they have anticancer and herbicidal applications. Schiff bases are active against a wide range of organisms for example *Candida Albicans, Escherichia coli Staphylococcus aureus, Bacillus polymxa, Trychophyton gypseum, Mycobacteria, Erysiphe graminis* and *Plasmopora viticola*.They serve as models for biologically important species. *O-phenylenediamine* Schiff bases show clinical properties[10,11] , Isatin Schiff bases were reported to possess antiviral, anti-HIV, anti protozoal and anthelmintic activities[12] , Schiff bases derived from 4-dimethylamine benzaldehyde shows antifungal activity,In medicines used as antibodies and anti-inflammatory agents[13] .

Experimental

Materials

All chemicals used in this investigation were reagent of BDH or Aldrich including, 2-hydroxy-1-napthylaldehde , m-phenylenediamine , EtOH, DMF, ether.

Synthesis of Schiff base

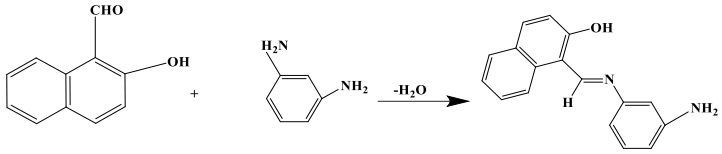
The Schiff base **(**E)-1-(((3-aminophenyl)imino)methyl)naphthalene-2-ol was synthesized by refluxing 50ml ethanolic solution (8.609g, 0.05mmol) of 2-hydroxy 1-napthylaldehde with 50ml ethanolic of m-phenylenediamine (5.407g, 0.05mmol)for three hours. The obtained product was allowed to cool at room temperature, filtered and washed with ether and recrystallized from ethanol, and kept in a desiccator over silica gel to get yellow precipitate (m.p. 162 ; yield 82%)

Synthesis of Complexes

The Schiff base complexes under investigation were synthesized by adding **(**E)-1-(((3-aminophenyl)imino)methyl)naphthalene-2-ol (2.62 g, 0.001mmole) in 30ml absolute EtOH to 0.01 mmole of the salts of $CrCl_3.6H_2O$ (2.66 g), $MnCl_2.4H_2O$ (1.97 g), in the same amount of the absolute EtOH. The reaction mixtures were heated under reflux for 3 hours. The complexes were filtered off, recrystallized from the suitable solvent and finally kept in a desiccator over silica gel.

RESULTS AND DISCUSSION:

The reaction between the 2-hydroxy-1-napthylaldehde and m-phenylenediamine yields only one product which is as follows:



Microanalysis and molar conductance measurements

The elemental analysis data and some physical properties of the Schiff base and its complexes are summarized in Table1 where the results confirm the proposed composition. The synthesized complexes were formed in 1:1 (M:L) ratio. the obtained molar conductance values of the complexes in DMF solvent lie in the range of 30 - 36 ohm^{-1} cm^2 mol^{-1} indicating their complexes of Cr^{3+}, Mn^{2+} are nonelectrolytic.

Table (1): Elemental analysis and some physical properties of the Schiff base(L) and its complexes

Ligand / complexes	M.wt	%Calc.(Found)			Λ (μs) ohm^{-1} cm^2 mol^{-1}	BM
		C%	H%	N%		
L $C_{17}H_{14}N_2O$	262.11	77.49(76.49)	5.14(5.25)	10.68(10.86)	-	-
$[Cr(L)(H_2O)_2(Cl)_2]$	420.23	48.59(49.11)	4.08(4.14)	6.67(6.48)	30	3.81
$[Mn(L)H_2OCl]$	369.71	55.23(55.51)	4.09(4.68)	7.58(6.88)	36	5.66

Mass spectrum of the Schiff base

The mass spectral data of the Schiff base ligand shown in figure 1. Mass spectrum of the ligand showed molecular ion peaks, which were in good agreement with the expected values[14]. The mass spectrum of ligand gives a peak at 262m/z.

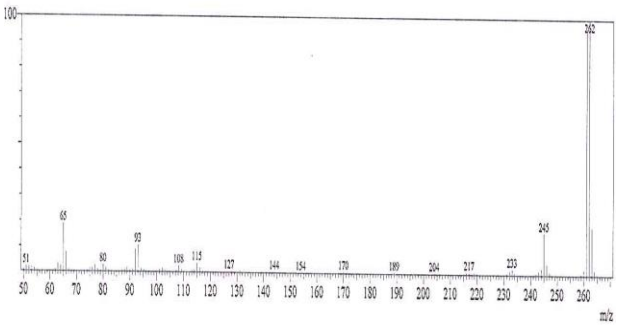


Fig.(1): Mass spectrum of Schiff base

Proton nuclear magnetic resonance spectrum of ligand

The ^{1}H-NMR spectrum recorded in d^6 DMSO solvent on a Jeol-90 Fourier Transform (200MHz). **(**E)-1-(((3-aminophenyl)imino)methyl)naphthalene-2-ol shows four singlet signals figure 2 at 5.809, 7.258-7.978, 9.604 and15.809, downfield of TMS, attributed to the protons of, NH_2, H(phenylring) , and OH respectively[15,16].

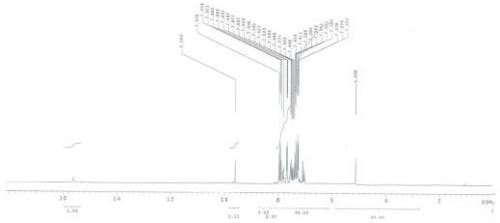


Fig.(2): ^{1}H-NMR spectrum of Schiff base

Electronic spectra

The electronic absorption spectra of the complexes under investigation were recorded using in Nujol mull on a Unicom model UV2 spectrophotometer (Figs. 3-5). The Schiff base ligand spectrum exhibits two absorption bands at 44444 cm^{-1}, 39062 cm^{-1}, attributed to π→π* and n→π* transitions respectively[17]. The chromium(III) complex spectrum exhibits absorptions at 44642 cm^{-1} attributed to π→π* transition, and show band at 22471 cm^{-1} which is due to $^3A_2g(F)\rightarrow{}^3T_1g(P)$ d-d transitions. An octahedral structure is suggested for Cr(III) complexes[18]. The electronic absorption spectrum of Manganese(II) complex exhibit absorption band at 42372 cm^{-1} due to π→π* transitions, and show band at 22624 cm^{-1} attributed to $^6A_1g^4\rightarrow T_1g(P)$ (d-d) transition, which indicates the presence of Mn(II) complex in tetraheral structure [19].

Table (2): IR and electronic spectral data of the Schiff base and its complexes

Ligand/ Complexes	IR (cm^{-1})				UV - Vis λ_{max} (cm^{-1})
	υOH	υC=N	υM-N	υM-O	
L ($C_{17}H_{14}N_2O$)	3448	1538	-	-	44444,39062 cm^{-1}
$[Cr(L)(H_2O)_2(Cl)_2]$	3862	1605	650	503	44642,22471 cm^{-1}
$[Mn(L)H_2OCl]$	3832	1598	603	545	42372,22624 cm^{-1}

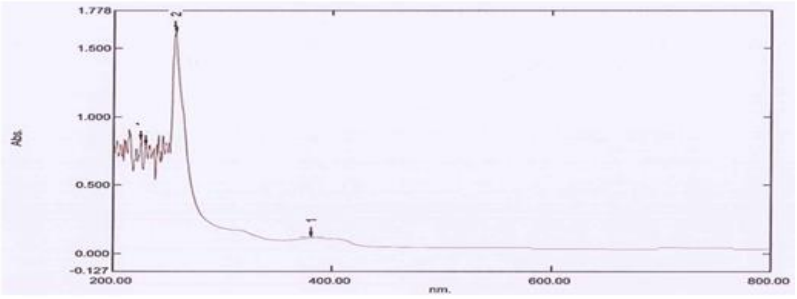


Fig.(3): UV spectrum of the free ligand L

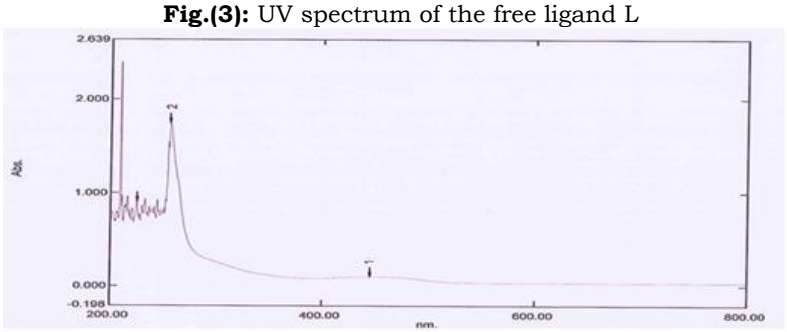


Fig.(4): Electronic spectrum of Cr(III) complex

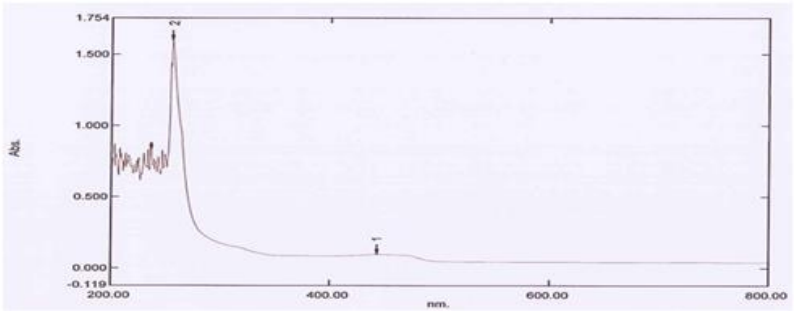


Fig.(5): Electronic spectrum of Mn(II) complex

Magnetic susceptibility measurements

The magnetic moment value of Cr(III) complex is 3.81 BM which suggests an octahedral geometry[20]. The magnetic moment of Mn(II) complex is 5.66 BM which suggests the high spin four-coordinated tetrahedral arrangement of the ligand around the metal ion[21].

IR spectra

The IR spectra of the ligand and its complexes with Cr^{3+}, Mn^{2+}were recorded in the solid state in the rang 400-4000 cm^{-1} using KBr disc on a Perkin-Elmer 1430 ratio recording infrared spectrophotometer (Figs. 8-10). The IR spectral data are present in Table2. A verification of the structures of the metal complexes can be easily achieved by comparing the IR spectrum of the free ligand with those of complexes[22]. When a Schiff base ligand is coordinated to metal ion at least one additional atom is introduced into the ligand vibrating system. It is thus expected that bond lengths, angles and interacting forces within the ligand would be altered even at least slightly. The IR spectrum of the Schiff base display two bands at 3448 cm^{-1} attributed to νOH group[23], and show a band at 1620 cm^{-1} attributed to C=N group[24]. The shifting of ν(C=N) group vibration in all complexes indicates the participation of nitrogen atom during chelates. Complexes IR spectrum display broad bands in the range of 3434-3862 cm^{-1} which is attributed to stretching vibration νOH of coordinated water molecules banding with complexes formation. the New bands observed at 498-550 cm^{-1} and at 560-650 cm^{-1} which could be attributed υ(M-O) and υ(M-N) vibrations respectively[25,26].

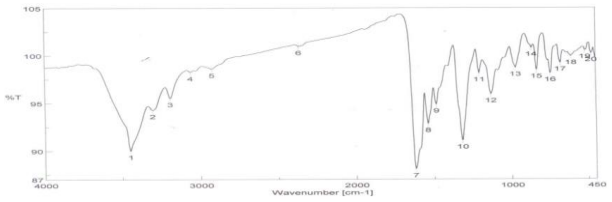


Fig.(8): IR spectrum of the Schiff base

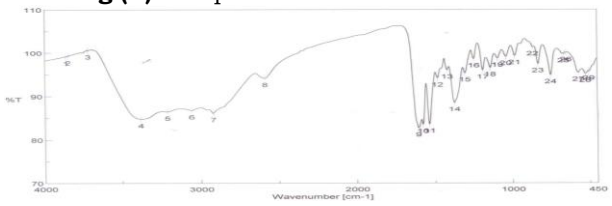


Fig.(9): IR spectrum of Cr(III) complex

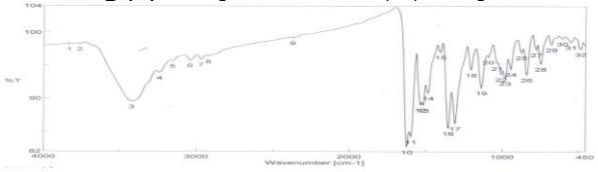
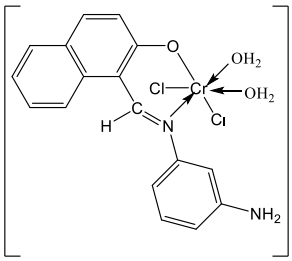


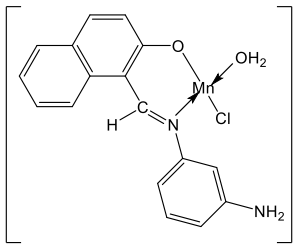
Fig.(10): IR spectrum of Mn(II) complex

Conclusion

On the basis of the analytical and spectral data, the synthesized chromium(III), manganese(II), Schiff base (L) complexes suggests 1:1 [ML] metal to ligand stoichiometry and exhibit octahedral and tetrahedral and are structures the ligand is coordinated to the metal ions as a tridentate and bidentate , the following geometrical structures of the synthesized complexes were suggested.



[Mn(L) H2O Cl]



$[Cr(L)(H_2O)_2(Cl)_2]$

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